

EARLY PRODUCTS OF PYROLYSIS OF WOOD

William F. DeGroot, Wei-Ping Pan, M. Dalilur Rahman, Geoffrey N. Richards

Wood Chemistry Laboratory, University of Montana, Missoula, Montana 59812 USA

INTRODUCTION

We are studying the first stages in pyrolysis of wood and other cellulosic materials as part of a study of the chemistry of smoldering or low-temperature combustion. In the latter processes both oxidative and non-oxidative pyrolysis occur. This paper describes an investigation of the first volatile products of pyrolysis of wood and we believe that many of the conclusions regarding the first pyrolysis reactions at low temperatures are applicable also to higher temperature treatments of wood such as are utilized in liquifaction processes. Our aim was primarily to determine the relative rates and modes of pyrolysis of the three major constituents of wood (viz. cellulose, hemicelluloses and lignin) from their chemically intact situation in whole wood. We believe that interactions of these substances and of their degradation products during pyrolysis make this approach necessary and may invalidate some aspects of earlier studies of pyrolysis of isolated wood fractions.

METHODS

Our major technique has been the coupling of a thermogravimetric analysis system (TG) with a Fourier transform infrared spectrometer. The coupling is by a heated 1 m. teflon tube from the TG to an infrared gas cell. All of the results were obtained with cottonwood sapwood (*Populus trichocarpa*) which had been ground to pass an 80 mesh sieve. All pyrolyses were carried out in flowing nitrogen, the time lag between the thermal balance and the gas cell was 1 min, and heating was either isothermal at 250°C or at 3°/min. from 100° to 500°. In the isothermal runs for periods up to 2 hrs. the whole infrared spectrum could be accounted for by the absorption bands of the 6 components shown in Table 1. The system was therefore calibrated for these compounds by heating the pure liquid in a loosely covered pan on the thermal balance at an appropriate temperature and relating the rate of weight loss to the infrared spectrum. Where a wavenumber range is shown in Table 1, the absorbance was integrated between these values and where a single wavenumber is given, the height of that Q branch was used. These values bore a linear relationship to the rate of weight loss for an individual compound, and the resultant calculated response factors were used to calculate the rates of production of each product from heated wood samples. For carbon dioxide the calibration was based on air versus a pure nitrogen blank and the carbon monoxide calibration was then deduced from a standard mixture of the two oxides in nitrogen.

The effects of cations on the pyrolyses were investigated with wood which had been washed with acid to remove all metal ions and with samples in which the indigenous cations had been replaced entirely with either potassium or calcium ions. These ion exchange processes caused no other chemical change in the wood. E.g. the content of L-arabinofuranose units (which comprise one of the most acid-labile groups in wood) was unchanged.

Total absolute glucose contents of the wood samples were determined by acid hydrolysis, reduction, acetylation and gas chromatography using i-inositol as internal standard (1). Uronic acids were determined on a aliquot portion of the hydrolyzates (2) and vanillin and syringaldehyde from lignin were generated by nitrobenzene oxidation (3) and determined by gas chromatography of trimethylsilyl ethers. The glucan components of the heated wood samples were very resistant to hydrolysis with 72% sulfuric acid and it was necessary to "reactivate" with water before hydrolysis.

RESULTS AND DISCUSSION

Figure 1 shows that the cations have a major influence on the rate of pyrolysis of wood. The results confirm earlier studies (4) and show that of the two major cations present in wood, potassium is dominant in catalysis of pyrolysis, whereas calcium tends to stabilize the wood towards pyrolysis. The low temperature inflection in the DTG curves at 250-300° has often been assumed to be associated with hemicellulose and/or lignin degradation and since the cations occur predominantly in the hemicelluloses (5) we have studied pyrolysis in this region in some detail by isothermal pyrolysis at 250°. Figure 2 shows the weight loss under such conditions and the rates of weight loss for original wood and for potassium-exchanged wood were indistinguishable. The weight loss curves for acid-washed and for calcium-exchanged wood were also indistinguishable, but corresponded to a much lower rate of pyrolysis.

The rates of formation of the volatile products determined by infrared spectroscopy are shown in Figure 3 for the original wood. Similar results are also available for the ion-exchanged woods. Table 2 shows the proportion of total weight loss in the wood sample that can be accounted for by the infrared analysis. The 40% of unaccounted weight loss represents material which condensed before reaching the infrared cell. This is likely to consist of a mixture of larger molecules containing two or more carbon atoms. It is evident that carbon dioxide and methanol are the first products of pyrolysis at 250°, very closely followed by water, which is the major product on either a weight or molar basis. Formic acid is produced steadily over a relatively long period, while acetic acid production peaks much later than the carbon dioxide, methanol and water. The changes in glycose, uronic acid, vanillin and syringaldehyde content are shown in Table 3. We conclude that the methanol is formed predominantly by pyrolysis of lignin with syringyl units pyrolysing rather more rapidly than guaiacyl. The amount of methanol released is much greater than could be accounted for by the 4-O-methylglucuronic acid units of the hemicelluloses. Evidently however, some units or regions of the lignin are especially labile; only about half of the available methanol is released in 1 hr. at 250°, possibly in two stages, and the remainder requires higher temperatures (see below). The carbon dioxide is evidently derived predominantly from decarboxylation of uronic acids which decrease rapidly in the solid residue and the molar yield of carbon dioxide corresponds approximately with the uronic acid content of the wood. Since the glucan content of the wood is virtually unchanged in 50 min. at 250°, it appears that cellulose survives this treatment, although it is quite likely that some chain scission will occur and perhaps some transglucosylation. The acetic acid is almost certainly released by pyrolysis of the acetyl ester groups from the xylan and its yield is approximately that anticipated from the acetyl content of the wood.

The water, which is the major product, must be formed predominantly from the hemicelluloses. Some water will obviously be formed from the uronic acid and arabinose units which decompose rapidly, but water must also be derived from xylose units which show some decrease. Since we would anticipate that the β -1,4-xylan chain should have a thermal stability similar to cellulose and since glucose does not decrease, it seems probable that some of the xylose units may be subject to rapid elimination reactions yielding water, particularly in the regions of the hemicellulose molecules in which uronic acids are decomposing. The pyrolysis of acetyl ester groups might also be associated with decomposition of the attached xylose units.

The mechanism of formic acid formation is not known. It could be derived from either hemicelluloses or lignin, although by analogy with its formation from polysaccharides by alkali degradation, the former seem more likely.

The influences of cations on yields of carbon dioxide, carbon monoxide (formed above 250°), methanol and formic acid during pyrolysis at temperatures up to 400° are shown in Figures 4-7. The yields of water and acetic acid were much less

sensitive to cation variation and are not shown. Figure 4 shows that the potassium ions favor increased formation of carbon dioxide and lower the temperature of peak production compared with the acid-washed or calcium forms. The total yield of carbon dioxide is much greater than could be explained by decarboxylation of uronic acids alone. The mechanism of formation of this carbon dioxide is not known. Since the bulk of the carbon dioxide is formed above 300° it must be derived at least partly from cellulose. Carbon monoxide was not significantly formed at 250°, but was produced in similar molar amount to carbon dioxide at higher temperatures, peaking at about 350° (Figure 7). It seems probable that this product also is largely produced from cellulose.

The formation of methanol (Figure 5) shows a distinct second peak at about 300° for original and for potassium-exchanged wood. Presumably the methanol evolved above 320° is catalyzed by potassium and derived by pyrolysis reactions from the more resistant lignin which survives pyrolysis at lower temperatures. Formic acid (Figure 6) evidently forms at higher temperatures by potassium catalyzed pyrolysis reactions from cellulose. The same acid is a major product of alkaline degradation of cellulose in absence of air and it is probable that the greater effectiveness of potassium compared with calcium in catalyzing formation of formic acid (and perhaps methanol) is associated with the greater basicity of the former.

REFERENCES

1. E.g., M.J. Neilson and G.N. Richards, Carbohydr. Res. 104 (1982) 121-138.
2. N. Blumenkrantz and G. Asboe-Hansen, Anal. Biochem., 54 (1973) 484-489.
3. B. Leopold and I.L. Malmstrom, Acta Chem. Scand., 6 (1952) 49-55.
4. W.F. DeGroot and F. Shafizadeh, J. Anal. Appl. Pyrol., 6 (1984) 217-232.
5. W.F. DeGroot, Carbohydr. Res., 142 (1985) 172-178.

Table 1. Infrared absorbances used to quantify the first volatile products from pyrolysis of wood and conditions used for calibration.

Compound	Wavenumbers (cm ⁻¹)	Temperature (°C)	Rate of Weight Loss (μg/min)
CO ₂	2240 - 2400	--	
CO	2020 - 2240	--	
CH ₃ COOH	1140 - 1230	23, 30	16, 32
H ₂ O	1653	23, 30	17, 61
HCOOH	1105	23, 26	12.6, 30.0
CH ₃ OH	1032	23, 30	42.6, 137

Table 2. Yield of volatile products by infrared detection as percentage of total weight loss; cottonwood at 250°C in nitrogen.

	<u>% of Total Weight Loss</u>			
Methanol	3.5	3.7	3.8	4.4
Formic acid	5.0	6.4	8.2	7.0
Acetic acid	7.5	15.5	19.0	23.0
Carbon dioxide	10.5	9.2	12.0	13.2
Water	<u>21.5</u>	<u>18.3</u>	<u>16.0</u>	<u>13.2</u>
Total	47.5%	53.1%	59.0%	60.8%
Time at 250°	11 min	23 min	40 min	58 min
Total weight loss	5.5%	8.0%	11.0%	12.5%

Table 3. Analyses of cottonwood after heating at 250°C under nitrogen.

Analysis (% dry weight)	Original Dry Wood	250°/N ₂ /50 min.
(Anhydroglycoses)		
Rhamnose	0.2	0
Arabinose	0.5	trace
Xylose	15.8	12.3
Mannose	3.0	2.4
Glucose	51.3	51.3
Uronic acid	4.9	1.7
Total Carbohydrate	75.7	67.7
Vanillin	2.7	1.8
Syringaldehyde	5.7	2.2
Weight loss	0	11.9%

FIG. 1
DTG
Cottonwood, N_2 , $3^\circ/\text{min}$.







